

PATENT SPECIFICATION

NO DRAWINGS

1,039,468



1,039,468

Date of Application and filing Complete Specification: July 22, 1963.

No. 28894/63.

Application made in France (No. 905056) on July 25, 1962.

Complete Specification Published: Aug. 17, 1966.

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Index at acceptance:—C2 C(1Q1A, 1Q6A1, 1Q6A2, 1Q8A, 1Q8B, 1Q8C, 1Q11A, 1Q11J)
Int. Cl.:—C 07 c 21/18

COMPLETE SPECIFICATION

**Improvements in and relating to the Preparation of
Vinylidene Fluoride**

We, PRODUITS CHIMIQUES PECHINEY-SAINT-GOBAIN a French Company of 63, rue de Villiers, Neuilly-sur-Seine, France, do hereby declare the invention, for which we

5 pray that a patent may be granted to us, and the method by which it is to be performed to be particularly described in and by the following statement:—

10 This invention relates to the preparation of vinylidene fluoride ($\text{CH}_2 = \text{CF}_2$).

15 The invention is concerned with an industrial process for making vinylidene fluoride which makes it possible to obtain this compound with a rate of transformation higher

than 80% and a yield which is practically quantitative. Furthermore the corrosive effects are almost non-existent through the use of the working conditions we have adopted which avoid the formation of hydrofluoric acid.

20 According to the invention we provide a process for preparing vinylidene fluoride which comprises heating a monobromo 1,1-difluoro-ethane to a temperature between 300° and 600°C., maintaining this bromodifluorinated

25 derivative within this temperature range for a period of time less than 60 seconds and then separating the products of the reaction in order to recover the vinylidene fluoride formed.

30 The invention, which is preferably carried out using 1-bromo-1,1-difluoro-ethane, is advantageously effected at a temperature in the range from 500°C. to 550°C., which temperature is maintained for a period which is less than 60 seconds and is preferably from 5 to 30 seconds.

35 The reaction products can then be treated according to conventional methods so as to eliminate and recover the hydrobromic acid formed and any untransformed bromodifluorinated derivatives, and so isolate the vinylidene fluoride formed.

40 Pyrolysis temperatures above 600°C. can be used, but the increasing importance of undesired secondary reactions, mainly dehydro-

fluorination and the dissociation of compounds present in the pyrolysis gas, substantially decreases the yield of vinylidene fluoride and necessitates the use of an apparatus which is resistant to the corrosive action of hydrofluoric acid. The use of a reaction temperature below 300°C. leads to a real decrease in the rate of transformation of the bromodifluorinated reactant into vinylidene fluoride.

50 We have discovered that temperatures between 500°C. and 550°C. make it possible to obtain rates of transformation which are at least equal to 80% while securing a very high degree of selectivity.

55 The stay of the reactants in the pyrolysis zone is not a critical factor of the reaction. However, if the stay is too long, it favours the dissociation of vinylidene fluoride and reduces the productivity of the installation, whereas very short times decrease the rate of transformation, thus necessitating the recycling of the untransformed reactant, and the consequent handling of large volumes of gases. These drawbacks have led us to prefer contact times ranging from 5 seconds to 30 seconds. The presence of a filler which is inert with respect to the reactants and to the products of pyrolysis does not substantially modify the results obtained.

60 70 The pressure does not have a preponderant influence on the rate of transformation and on the yield of the reaction. It is possible to work at high pressures or at pressures below atmospheric pressure, but it is preferred to use pressures which are near atmospheric pressure so as to simplify the installation, pressures between 0.5 and 2 atmospheres being convenient.

75 80 In a modification of the process, it is possible to use a direct reaction between 1,1-difluoro-ethane and bromine so as to have a molar ratio of bromine to difluoroethane which is slightly below 1, at a temperature ranging from 350°C. to 500°C., and preferably between 400°C. and 450°C., so as to form,

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5 *in situ*, a mixture of bromofluorinated derivatives which is transformed during the same operation into vinylidene fluoride by applying the process described above. The formation of the starting product together with its transformation into vinylidene fluoride may be carried out either in one reactor or in two separate reactors.

10 The following examples are given solely by way of illustration of the invention.

EXAMPLE 1

15 A reactor which is essentially constituted by a tube of "Pyrex" glass ("Pyrex" being a Registered Trade Mark) with an internal diameter of 4 cm. and 40 cm. long, and loaded with glass pellets with a 0.5 cm. average diameter, is placed in an electric furnace provided with a thermostat adjusted so as to maintain a temperature of 530°C. over a length 20 of about 20 cm. of the central part of the tube. A gaseous flow of 1-bromo-1,1-difluoro-ethane ($CF_2Br - CH_3$) equal to 0.53 mole hour is fed at atmospheric pressure into the pyrolysis tube, and the flow corresponds to a 25 contact time of about 15 seconds (calculating

30 the space velocity of the reactant under the conditions of the reaction, namely at 530°C.). At the outlet of the reactor, the gases are washed with water and then with an aqueous solution of dilute caustic soda, and are then dried on a calcium chloride column. The unreacted 1-bromo-1,1-difluoro-ethane is condensed in a first container cooled with brine; the crude vinylidene fluoride is condensed in a condenser cooled at the temperature of liquid nitrogen. It is then distilled in a column the condenser of which is cooled with liquid air.

35 The rate of transformation of the bromofluorinated derivative is equal to 80 mole per cent and the yield in vinylidene fluoride is equal to 99.5 mole per cent; this gives a conversion rate of 79.5%.

EXAMPLE 2

40 The following table shows, as a basis of comparison and to make clearer the advantages of our new process, the results obtained when submitting 1-chloro-1,1-difluoro-ethane ($CF_2Cl - CH_3$) to pyrolysis in a copper tube under 45 conditions similar to those described in Example 1 above.

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	$CF_2Cl - CH_3$		$CF_2Br - CH_3$
<i>Reactor</i>			
Material	copper		"Pyrex" glass
Internal diameter (mm)	40		40
Heated length (cm)	40		40
<i>Filling</i>	none	Raschig rings	Glass pellets
Flow rate of the reactant (mole/h)	0.39	0.40	0.55
Temperature in °C: walls of reactor	620°	590°	530°
" " " centre of reactor	550°	550°	500°
Rate of transformation (mole %)	54.2	48.8	79.8
Rate of conversion of the reactant in vinylidene fluoride (mole %)	53	47	79.5

Remarks Favourable catalytic influence of the wall and of the filling. Formation of HF and $CFCl=CH_2$. Risks of clogging through formation of copper chloride and tar.

Operating conditions identical to Example 1. No trace of attack on the reactor.

"Pyrex" is a Registered Trade Mark.

EXAMPLE 3

5 The reactor used is a tube made of "Pyrex" glass with a 20 mm. internal diameter and 120 cm. long, heated homogeneously along about 100 cm. With a flow rate of 1-bromo-1,1-difluoro-ethane equal to 1 mole/hour, at a temperature near to 550°C. and a contact time below 60 seconds, the rate of

transformation is equal to 81.2% and the yield in vinylidene fluoride is practically quantitative (99.7%). The rate of conversion is 81%.

10 The table below shows clearly the advantages of the process based upon the pyrolysis of the bromine derivative in comparison with the prior art.

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	CF ₂ Cl - CH ₃	CF ₂ Br - CH ₃
<i>Reactor</i>		
Material	Copper	"Pyrex" glass
Internal diameter (mm)	20	20
Heated length (cm)	100	100
Filling	none	none
Flow rate of the reactant mole/h)	0.9	1.0
Temperature of the heated zone (°C)	630	550
Rate of transformation (mole %)	16.0	81.2
Rate of conversion of the reactant into vinylidene fluoride (mole %)	15.8	81
Remarks	Same as Example 2	—

"Pyrex" is a Registered Trade Mark.

WHAT WE CLAIM IS:—

20 1. A process for preparing vinylidene fluoride which comprises heating a mono-bromo 1,1-difluoroethane to a temperature between 300° and 600°C., maintaining this bromodifluorinated derivative within this temperature range for a period of time less than 60 seconds and then separating the products of the reaction in order to recover the vinylidene fluoride formed.

25 2. A process as claimed in claim 1, in which the reaction period is within the range of from 5 to 30 seconds, inclusive.

30 3. A process as claimed in claim 1 or claim 2, in which the temperature range is between 500° and 550°C.

35 4. A process according to any of the preceding claims in which the heating is effected under a pressure which is substantially between 0.5 and 2 atmospheres.

40 5. A process as claimed in any of the preceding claims, in which 1,1-difluoro-ethane and bromine are reacted together in a molar ratio of bromine to difluoroethane which is just below 1 and at a temperature within the range

of from 350°C. to 500°C., to form, *in situ*, a mixture of bromofluorinated derivatives, and in which the mixture of bromofluorinated derivatives is then heated to a temperature between 300° and 600°C. to form vinylidene fluoride in the same reactor or in a further reactor.

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6. A process as claimed in claim 5, in which the temperature is within the range of from 400°C. to 450°C. during the bromination reaction.

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7. A process for preparing vinylidene fluoride as claimed in claim 1 and substantially as herein described and with reference to the examples given.

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